XIX. *Experiments on the Congelation of Quickſilver in* England. *By Mr.* Richard Walker; *in a Letter to* Henry Cavendiſh, *Eſq. F. R. S.*

Read May 28, 1789.

SIR,

I NOW beg leave to trouble you with the particulars of my experiments relative to the congelation of mercury; to which I ſhall add an account of a few experiments, relating to the production of artificial cold, made ſince my laſt Paper was written.

Exp. 1. On December 28th laſt, a favourable opportunity offered of beginning ſome experiments on the congelation of mercury, which I was deſirous of effecting completely; how far I have ſucceeded will appear in the ſequel.

For this purpoſe I prepared a mixture of diluted vitriolic acid (reduced by water till its ſpecific gravity was to that of water as 1,5596 to 1) and ſtrong fuming nitrous acid, of each equal parts. I preferred this mixture of acid becauſe it has been found by Mr. Mc NAB, in Hudſon's Bay, to be capable of producing much greater cold, when the temperature of the materials at mixing is very low, than the nitrous acid alone; the former ſinking a ſpirit thermometer to $-54°\frac{1}{2}$, the latter never lower than $-46°$.

The glaſs tube of a mercurial thermometer, with its bulb half filled with mercury, was provided, this occurring to me

as a convenient method of aſcertaining when the mercury was congealed; for if, after being ſubjected to the cold of a frigorific mixture, the thermometer glaſs ſhould be taken out and inverted, and the mercury found to remain completely ſuſpended in that half of the bulb now uppermoſt, no doubt can remain of the ſucceſs of the experiment; an hydrometer, with its lower bulb half an inch in diameter, and three-fourths full of mercury, was likewiſe provided, in caſe any accident ſhould happen to the other.

It may be proper to premiſe here, that in all experiments of this kind I remove each veſſel, when the liquor it contains is ſufficiently cooled, out of the mixture in which it is immerſed for that purpoſe, immediately previous to adding the ſnow or ſalts with intention to generate a ſtill further increaſe of cold; and likewiſe prefer adding the ſnow or powdered ſalts to the liquor, inſtead of pouring the liquor upon theſe: it is neceſſary alſo to ſtir about the ſnow or ſalts, whilſt cooling in a frigorific mixture, from time to time, otherwiſe it will freeze into a hard maſs, and fruſtrate the experiment.

A half-pint glaſs tumbler, containing two ounces and a half of the above-mentioned diluted mixture of acids, being immerſed in mixtures of nitrous acid and ſnow, until the liquor it contained was cooled to $-30°$, was removed out of the mixture and placed upon a table; ſnow, likewiſe previouſly cooled in a frigorific mixture to $-15°$, was added by degrees to the liquor in the tumbler, and the mixture kept ſtirring until a mercurial thermometer ſunk to $-60°$, where it remained ſtationary; the hydrometer was then immerſed in the mixture (the thermometer glaſs having been broken in the courſe of the experiment), and ſtirred about in it for a ſhort time, and on taking the hydrometer out, and gently ſhaking it, I

perceived the mercury had already acquired the conſiſtence of an amalgam, and after immerſing it again for a few minutes, and then taking out and inverting it, I was gratified for the firſt time with the ſight of mercury in a ſtate of perfect congelation. I applied my hand to the inverted glaſs bulb; this ſoon looſened the ſolid mercury, which, on ſhaking the hydrometer, was diſtinctly heard to knock with force againſt the glaſs; it was then immerſed a ſecond time, and when taken out was found adhering to the glaſs as before. I now inverted the glaſs again, and kept it in that ſituation until the whole of the mercury melted, and dropped down globule after globule into the ſtem of the hydrometer. The interval of time from taking the mercury out of the frigorific mixture in a ſolid ſtate, the laſt time, to its perfect liquefaction, was not noticed; but, upon recollection immediately afterwards, was ſuppoſed to be not leſs than three or four minutes. In a ſucceeding experiment this circumſtance was attended to, and the frozen mercury, weighing ſeven ſcruples, was not entirely melted under ſeven minutes, the temperature of the air + 30°.

The experiment which follows I conſider the moſt extraordinary, becauſe it proves beyond a doubt, that mercury may be frozen not only here in ſummer, but even in the hotteſt climate, at any ſeaſon of the year, by a combination of frigorific mixtures, in the way deſcribed in the Philoſophical Tranſactions, Vol. LXXVII. p. 285. in which attempt to freeze mercury, made April 20, 1787, the temperature of the air and materials being + 45°, I certainly reached (without the aſſiſtance of ſnow or ice) the point of mercurial congelation; but had then no ſatisfactory proof that any part of the mercury was abſolutely congealed.

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Exp. 2. On December 30. three ounces of a mixture compoſed of ſtrong fuming nitrous acid two parts, and ſtrong vitriolic acid and water each one part, were cooled in a half pint tumbler immerſed in a frigorific mixture, till the temperature of the diluted mixture of acids was reduced to $-30°$. The tumbler was then removed out of the mixture, and vitriolated natron (GLAUBER's ſalt) in very fine powder, previouſly cooled to $-14°$ by a frigorific mixture, added by degrees to the liquor in the tumbler, ſtirring it together until the mercury in the thermometer ſunk to $-54°$. The hydrometer uſed in the former experiment, with its lower bulb three-fourths full of mercury, was now immerſed and ſtirred about in the mixture for a few minutes, when on taking it out, and inverting it, I had the ſatisfaction to find the ſame proof of the mercury being frozen as in the former inſtance. It was immediately ſhewn to the gentlemen preſent, who expreſſed likewiſe their entire ſatisfaction. Nearly four ounces of the powdered ſalt was added; but, I believe, ſome was added after the greateſt effect was produced. I had no nitrated ammonia by me, otherwiſe I ſhould have uſed upon this occaſion, inſtead of vitriolated natron alone, a mixture of theſe two ſalts in powder, in the proportion of ſeven parts of the former to eight of the latter. The temperature of the room in which theſe experiments were made was $+30°$ each time, and the mercury taken from a jar containing ſeveral pounds.

Exp. 3. By an experiment made purpoſely on January 10. laſt, at which Dr. BOURNE was preſent, I have found that mercury may be congealed tolerably hard, by adding freſh fallen ſnow, at the temperature of $+32°$, to ſtrong fuming nitrous acid, previouſly cooled to between $-25°$ and $-30°$, which may be very eaſily and quickly effected by immerſing

the veſſel containing the acid in a mixture of ſnow and nitrous acid.

I uſe the *fuming* nitrous acid upon all occaſions, becauſe that does not require to be diluted, cold being immediately produced on the ſmalleſt addition of ſnow.

Exp. 4. On January 12, at Dr. THOMSON's requeſt, I repeated the experiment of freezing mercury, at the Anatomy School in Chriſt Church, in the preſence of the honourable Mr. WENMAN, the rev. Dr. HOARE, Dr. SIBTHORP, junior, Dr. THOMPSON, the rev. Mr. JACKSON of Chriſt Church, and Mr. WOOD of this place, a gentleman well known for his ingenuity in mechanics.

For this purpoſe were provided a ſpirit thermometer graduated very low, and a mercurial thermometer graduated to $-76°$, two thermometer glaſſes, with bulbs very near, if not quite, an inch in diameter each, one filled with mercury nearly to the orifice of the tube, which was left open, the other with its bulb half filled, and an hydrometer with its lower bulb (conſiderably leſs than either of the others) likewiſe half filled with mercury; the temperature of the room at this time $+28°$.

A pan, containing nine ounces of the mixture of acids prepared as in the firſt experiment, was placed in a larger pan, containing nitrous acid, and this, in a frigorific mixture of nitrous acid and ſnow, contained in another pan much larger. When the nitrous acid in the ſecond pan was cooled by this mixture to $-18°$, and the mixed acids in the ſmalleſt pan nearly as much, ſnow at ſomewhat between $+20°$ and $+25°$, the temperature of the open air at that time, was added to the nitrous acid in the ſecond pan, until the ſpirit thermometer ſunk to near $-43°$; then the thermometer, with its bulb half filled, was immerſed a ſufficient time, and when taken out,

out, the mercury in it was found congealed, and adhering to the glaſs. The pan containing the mixed acids, and which had been removed whilſt the ſnow was added to make the ſecond mixture, was now replaced in it, in order to be cooled; and when the mixture of acids was reduced to the temperature of $-34°$, ſnow previouſly cooled to $-18°$ was added, keeping the mixture ſtirred until the mercurial thermometer ſunk to $-60°$; its temperature by the ſpirit thermometer was then found to be $-51°$.

The three glaſſes containing the mercury to be frozen were now immerſed in this mixture, and having been moved about in it for a conſiderable time, during which the ſpirit thermometer roſe ſcarcely one degree, were then ſeverally taken out and examined.

As the examination of the frozen mercury was more immediately under the inſpection of Dr. THOMSON, I ſhall tranſcribe here that gentleman's account of the phænomena.

"When the freezing mixture was ſuppoſed to have produced its effect, the bulb which was completely filled was taken out, and broken on a flat ſtone by a moderate ſtroke or two with an iron hammer. This bulb was eleven or twelve lines in diameter.

The ſolid mercury was ſeparated into ſeveral ſharp and brilliant fragments, ſome of which bore handling for a ſhort time before they returned to a fluid form. One maſs, larger than the reſt, conſiſting of nearly one-third of the whole ball, afforded the beautiful appearance of flat plates, converging towards a center. Each of theſe plates was about a line in breadth at the external ſurface of the ball, becoming narrower as it ſhot inwards. Theſe facets lay in very different planes, as is common in the fracture of any cryſtallized ball, whether

whether of a brittle metal or of the earths, as in balls of calcareous ſtalactite. The ſolid brittle mercury in the preſent inſtance bore a very exact reſemblance, both in colour and plated ſtructure, to ſulphurated antimony, and eſpecially to the radiated ſpecimens from Auvergne, before they are at all tarniſhed.

Inſtead of a ſolid center to this ball, it ſeemed as if there had been a central cavity, of about two lines in diameter, a conſiderable portion of which was evident in the fragment juſt deſcribed, at that part to which the radii converged. It is indeed poſſible, that this may have been merely the receptacle of ſome part of the mercury remaining fluid at the center. The hollow within was ſhining, but its edges were neither ſoft nor mouldering; on the contrary, they were ſharp and well defined: nor was the brilliancy of the radii attributable to any exudation of mercury as from an amalgam.

In the two ſmaller bulbs, which were only half filled, the mercury preſerved its uſual luſtre on the ſurface in contact with the glaſs, as well as on that ſurface which it had acquired in becoming ſolid. The latter was occupied by a conical depreſſion, the gradations of which were marked by concentric lines.

One of theſe hemiſpheres was ſtruck with a hammer, as in the former inſtance, but was rather flattened and cruſhed than broken. The other, on being divided with a ſharp chiſſel, ſhewed a metallic ſplendour on its cut ſurface, but not equalling the poliſh of a globule of fluid mercury."

Thirteen ounces of ſnow in the whole were found to have been added to the mixed acids; but ſome was added to lower its temperature after the glaſſes containing the mercury were taken out, and the ſpirit thermometer had riſen a few degrees.

This was a day remarkably favourable for ſuch an experiment. My thermometer expoſed to the open air ſtood, at three quarters paſt eight this morning, at $+6°$, which is a very extraordinary degree of cold here; but this experiment was not begun till noon.

Exp. 5. On Jan. 14. I froze mercury at the Anatomy School again, in the preſence of the rev. the Dean of Chriſt Church, the rev. Dr. HORNSBY, and Dr. THOMSON.

Four ounces now of the mixture of acids, prepared as in the firſt experiment, were cooled in a tumbler to $-20°$, which required ſomewhat more than an equal weight of ſnow, cooled nearly to the ſame temperature, to produce the greateſt effect. This was ſomewhat leſs than in the laſt experiment, the ſpirit thermometer ſinking no lower than $-46°$, owing chiefly to the weather having become much warmer, the temperature of the open air being now $+36°$. The mercurial thermometer immerſed in this mixture ſunk to $-55°$, where it became ſtationary; then two thermometer glaſſes, one half filled with mercury, and the other filled to a conſiderable height up the the tube, after being immerſed ſome time, were examined. Upon breaking the ſhell of glaſs from the former of theſe, the mercury was found in a perfectly ſolid ſtate; but its upper ſurface, which was highly poliſhed, and of the colour of liquid mercury, inſtead of being only ſlightly depreſſed, as had been ſeen in every other inſtance which afforded an opportunity for inſpection, now formed a perfectly inverted hollow cone. This great depreſſion, as well as the concentric circles mentioned in a former inſtance, I ſuppoſe, might be owing to a rotatory motion accidentally given to it whilſt congealing. The ſolid mercury was beaten out, but having been ſuffered to lie ſome time on the table for inſpection, very quickly

melted into liquid globules. The flexibility of ſolid mercury was clearly to be obſerved in this beautiful ſpecimen; for the external ſurface, particularly the upper thin rim of the concave part, was evidently bent by the firſt gentle ſtroke of the hammer. The globe of mercury in the other glaſs, which was very ſmall, exhibited nearly the ſame phænomena, as in the inſtances before mentioned.

It happened in theſe experiments of mine, contrary to what has generally occurred to others, that the mercury never ſunk lower than $-60°$, ſeldom ſo low, in the thermometer, and but little below the point of mercurial congelation in the tubes of the thermometer glaſſes filled nearly up to the orifice, with a view to ſhew the contraction of mercury in becoming ſolid by its great deſcent in the tube. On reflecting on this circumſtance afterwards, it occurred to me, that the further deſcent of the mercury in theſe experiments was prevented not ſolely by the mercury freezing in the tube, the cauſe commonly aſſigned, but rather by the quick formation of a ſpherical ſhell of ſolid mercury within the bulb, by the ſudden generation of cold.

Dr. Beddoes expreſſing a deſire to exhibit ſolid mercury at his Lecture before his Claſs, I undertook to freeze ſome at the Laboratory on March 12th laſt, and now reſolved to ſatisfy myſelf reſpecting the cauſe which prevented the lower deſcent of the mercury in my former experiments. In this, as well as the former, the mercury in a thermometer graduated to $-60°$, and likewiſe in a thermometer glaſs, filled nearly to the orifice, which lengthened its ſcale to near $-250°$, ſunk only a few degrees below the point of mercurial congelation, and then remained ſtationary. After waiting ſome time, I took the thermometer out of the mixture, and obſerved the bulb apparently full, and the ſhort thread of mercury above unbroken.

I now embraced the lower part of the tube with my hand a few ſeconds, reſting it upon the upper part of the bulb; and upon taking it away, I found that the whole of the mercury had ſubſided into the bulb, which it did not now quite fill, a ſmall ſpace at the top of the bulb remaining empty. I then took out the thermometer glaſs, and applied my hand to the tube; but the mercury remained ſtationary until I ſunk my hand ſo as to communicate heat to that part of the bulb which is immediately connected with the tube, when the thread of mercury dropped entirely into the bulb. It was now immerſed again for a ſhort time, then taken out, and the ſhell of glaſs beaten off, which expoſed a globe of ſolid mercury, nearly an inch in diameter. This bore ſeveral very ſmart ſtrokes with a hammer before it began to liquify, but was not perfectly malleable.

In the courſe of theſe experiments, ſeveral fragments of the ſolid mercury were thrown into mercury in its ordinary liquid ſtate, and were found to ſink with conſiderable celerity.

In continuing my reſearches reſpecting the means of producing artificial cold, I have found that phoſphorated natron produces rather more cold by ſolution in the diluted nitrous acid than the vitriolated natron.

At the temperature of $+50°$, four parts of the diluted nitrous acid (prepared by mixing ſtrong nitrous acid with half its weight of water) required eight parts of that neutral ſalt in fine powder to be added, in order to cauſe the thermometer to ſink to $-6°$; and again, by the addition of five parts of nitrated ammonia in fine powder, the thermometer ſunk ſo low as $-16°$, in the whole ſixty-ſix degrees.

A mixture of this kind made the thermometer ſink from 80° (the temperature of the materials before mixing) to 0°.

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I was directed to the trial of this ſalt, by the like remarkable ſenſation of coldneſs without pungency, which, with its other ſimilar properties to ice, firſt induced me, whilſt purſuing the ſubject of cold, to try the effect of diſſolving the vitriolated natron in the mineral acids.

Equal quantities, by weight, of phoſphorated natron and vitriolated natron, were evaporated ſeparately over a gentle fire, until each was reduced to a perfectly dry powder. I then weighed them, and found the reſiduum of the phoſphorated natron ſomewhat lighter than that of the vitriolated natron; from whence it is probable the former contains the greateſt quantity of water of cryſtallization.

I have found, that each of the neutral ſalts which produce any remarkable degree of cold by ſolution in the mineral acids, *viz.* phoſphorated natron, vitriolated natron, and vitriolated magneſia, loſe this property entirely, when deprived by any means of their water of cryſtallization.

A ſhort time after I had firſt ſucceeded in freezing water in ſummer, by one mixture compoſed of three different ſalts in water (having been induced to try the effect of ſuch a method, from the conſideration that water, already ſaturated with one kind of ſalt, will diſſolve a portion of another, and after that a third, or even more), I met with the account of an experiment made by M. HOMBERG, related in one of the earlier Volumes of the Philoſophical Tranſactions, in which it is ſaid he produced an extraordinary degree of cold, by pouring a pint and a half of diſtilled vinegar upon two pounds of a powder compoſed of equal parts of crude ſal ammoniac and corroſive ſublimate, and ſhaking them well together. I immediately (July 30, 1786) prepared a mixture of this kind in ſmaller quantity, but found it produced only thirty-two degrees of cold,

cold, the temperature of the air and materials before mixing being 63°; which is no more than I have found may be effected by a ſolution in water of crude ſal ammoniac alone, previouſly dried and powdered.

By a trial made with great accuracy, I find, that even the mixture compoſed of diluted vitriolic acid and vitriolated natron is adequate to any uſeful purpoſe that may be required in the hotteſt country; for, by adding eleven parts of the ſalt in fine powder to eight parts of the vitriolic acid diluted with an equal weight of water, the thermometer ſunk from 80°, the mean temperature of the hotteſt climate, and to which theſe materials were purpoſely heated before mixing, to rather below 20°.

Vitriolated natron, added to the marine acid undiluted, produces very nearly as great a degree of cold as when mixed with the diluted nitrous acid. At the temperature of 50°, two parts of the acid, require three parts of the ſalt in fine powder, which will ſink the thermometer to 0°; and if three parts of a mixed powder, containing equal parts of muriated ammonia and nitrated kali, be added afterwards, the cold of the mixture will be increaſed a few degrees more.

The frigorific mixture above deſcribed, compoſed of phoſphorated natron and nitrated ammonia diſſolved in the diluted nitrous acid, being the moſt powerful, it will probably be found moſt convenient for freezing mercury, when ſnow is not to be procured. The materials for this purpoſe may be previouſly cooled in mixtures made of marine acid with vitriolated natron, muriated ammonia, and nitrated kali, in the proportions mentioned above, this being much cheaper than thoſe made with diluted nitrous acid, and very nearly equal in effect.

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In my laſt Paper I mentioned a freezing mixture, made by diſſolving a powder compoſed of equal parts of muriated ammonia and nitrated kali in water, and therein directed ſix parts of the mixed powder to be added to eight parts of water; but I have found ſince, that the beſt proportions are, five parts of the former to eight of the latter, by which I have ſunk the thermometer from 50° to 11°.

Having now proſecuted my ſubject relative to mixtures for generating artificial cold without the uſe of ice, from a poſſible method propoſed by Dr. WATSON (Eſſays, Vol. III. p. 139.), for freezing water in ſummer in this climate, and carried it on to a certain method of freezing, not only water, but even mercury, in the hotteſt climate, I now intend to take my leave of it.

I have the honour to be, &c.

RICHARD WALKER.